

REMARKS/ARGUMENTS

Reconsideration is respectfully requested of the Official Action of April 24, 2008, relating to the above-identified application. A one month extension of time, together with the fee associated therewith is filed herein.

Claim 1 has been amended to delete molybdenum from the list of elements (M) forming the mixture of both oxides and sulfides that are contemplated as an active promoter in the manufacture of the methylmercaptan as defined therein. Claims 7 and 8 have been deleted and the features thereof have been introduced into Claim 1.

The number of minor editorial amendments have also been made.

New Claim 41 is based on Claim 1 and defines the active promoter as a cerium oxide, cerium sulfide or cerium oxide and cerium sulfide and, optionally, a carrier.

No new matter is presented.

An extra fee for the additional independent claim is submitted herewith.

The rejection of Claims 1 to 4, 13, 16, 17, and 27 under 35 U.S.C. § 102(a) or (b) in view of the article by *Wang, et al., Ziran Kexueban* (2003), 42(1), 64-68 is traversed and reconsideration is respectfully requested. A complete copy of the article is enclosed herewith as provided by applicants. It will be noted that the reference is completely silent on the use of a promoter which is a mixture of oxides or sulfides or sulfides and oxides of an element (M) where (M) is selected from the group consisting of iron, cobalt, nickel, lanthanum, cerium and manganese.

The cited article of *Wang, et al.*, indicates that the activity of the promoter component decreases from cobalt oxide to nickel oxide to iron oxide. Applicants have determined, as shown by Table 3 in the present application, that the combination of iron and nickel which is catalyst (B) has a higher yield than the use of the cobalt catalyst (A) alone.

Regarding the differences in yield between catalyst (B) and catalyst (A) the MC (Methylmercaptan) yield increases from 0.47 (A) to 0.54 (B). This is an unexpected increase of about 13% related to the desired product. Therefore, the use of catalyst (B) leads to a significant advantage in the commercial use of the invention.

Consequently, applicants submit that an unexpected result has been obtained and discovered by using a mixture of the promoter oxides/sulfides as defined in Claim 1. Accordingly, since the *Wang, et al.*, article does not describe the use of a mixture of the defined elements, applicants respectfully submit that the rejection on the ground of anticipation should be withdrawn.

The rejection of Claims 1 to 4, 13, 16, 17 and 27 under 35 U.S.C. § 102(a) as anticipated by *Yiquan, et al.* (CN 1528516, hereinafter referred to as "CN '516") is traversed and reconsideration is respectfully requested. The CN '516 reference discloses the presence of an active accelerant in combination with the Mo-O-K catalyst where the active accelerator is mainly a transition metal or a rare earth oxide. However, there is no disclosure of the use of a promoter which is a mixture of oxides and/or sulfides of the metals defined in applicants' Claim 1 and,

therefore, applicants respectfully submit that the reference fails to anticipate the claimed invention.

In addition, applicants file herewith a translation of the applicants' three foreign priority documents in order to remove the reference as an effective reference against this application.

The Chinese application 2003101004961 discloses a catalyst and process for synthesis of methylmercaptan from synthesis gas ($\text{CO} + \text{H}_2$) containing a high concentration of hydrogen sulfide. The catalyst includes a solid carrier such as silica and Mo-O-K based complex as an active component. See Claim 1, page 3, lines 9-13.

The Chinese application 2003101004957 discloses a catalyst and process for synthesis in a single step of methylmercaptan from synthesis gas containing high concentration of hydrogen sulfide. The catalyst is Mo-O-K. A promoter is also present which can be a transition metal such as Fe, Mn, Co, Ni, La or Ce; see Claims 1-2. The reaction conditions of elevated temperature and pressure are described on page 6, lines 29, *et seq.*

The Chinese application 2004100083778 discloses a catalyst and process for synthesis of methylmercaptan from synthesis gas containing a high concentration of hydrogen sulfide in the presence of a Mo-O-K active ingredient carrier and one or more promoters including transition metals and/or cerium oxide; see Claim 1.

The rejection of Claims 1 to 4, 13, 16, 17 and 27 under 35 U.S.C. § 102(b) as anticipated by the article authored by *Yang, et al., Catalysis Letters* (2001), Vol. 74, No. 3-4, is traversed and reconsideration is respectfully requested. *Yang, et al.*, do not disclose the use of a mixture of

promoter materials to be used in combination with the main catalyst in accordance with the definition of the process recited in the rejected claims. Consequently, since *Yang, et al.*, do not describe the claimed invention, the reference fails under 35 U.S.C. § 102(b) as an anticipation and applicants respectfully request that the rejection be withdrawn.

The rejection of Claims 5 to 12, 18 to 26, 28 and 30 to 32 under 35 U.S.C. § 103(a) as unpatentable over the *Wang* article (2003), 42(1), 64-68 or *Yiquan, et al.*, CN '516 or the article by *Yang, et al.*, *Catalysis Letters* (2001), further in view of *Buchholz* (GB 2 016 468) is traversed and reconsideration is respectfully requested. None of the main references; namely, *Wang, et al.* (2003) or CN '516 or *Yang (Catalysis Letters)* teaches or suggests the use of a combination of promoter elements as defined in the claims of the present application for the synthesis of methylmercaptan.

The British patent of *Buchholz* does not provide the missing guidelines whereby a person skilled in the art would be led to the combination of components whereby as applicant has demonstrated in Table 3, unexpected improvements are obtained in terms of the yield of the desired product. In fact, applicants' data in Table 3 shows that catalyst (B) which is a combination of iron and nickel oxides, obtains superior results in terms of yield compared with the use of catalyst (A) which uses as a co-catalyst the cobalt material alone. A person skilled in the art could not have predicted the unexpected results in terms of improved yield when using a mixture of materials as a promoter. Therefore, applicants respectfully submit that the record

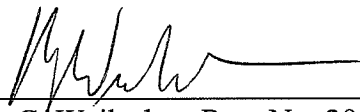
App. No. 10/595,333
Amend. dated Aug. 25, 2008
Resp. to OA of Apr. 24, 2008

herein shows that unexpected results are obtained and, accordingly, the rejection in terms of obviousness of the claimed invention should be withdrawn.

Favorable action at the Examiner's earliest convenience is respectfully requested.

Respectfully submitted,

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UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the Chinese and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in China on March 12, 2004 under the number 2004100083778 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group Ltd

The 7th day of July 2008

PCT / EP200 4 / 010872

11 November 2004

CERTIFICATE

The appendix to this certificate is a copy of the following patent application submitted to this office

Received 06 December 2004

WIPO PCT

Date of filing: 12.03.2004

Application No.: 2004100083778

Type of application: invention

Title of invention / creation: A catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide

Applicant: Xiamen University

Inventors or designers: Yang Yiquan, Wang Qi, Dai Shenjun, Yan Xingguo, Chen Aiping, Zheng Quanxing, Fang Weiping, Yuan Youzhu, Zhang Hongbin

Priority

Document

Submitted or transmitted in compliance
with Rule 17.1 (a) or (b)

Commissioner of the State Intellectual Property Office
of the People's Republic of China: Wang Jingchuan

11 October 2004

Claims

1. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide, characterized in that the said catalyst comprises an active ingredient, promoter and carrier, the said active ingredient being an Mo-O-K based complex, the promoter being at least one oxide of a transitional metal and/or cerium oxide, and the carrier being SiO₂; the said active ingredient Mo-O-K based complex is obtained by the conversion of the precursor K₂MoO₄ and is calculated as K₂MoO₄ or is converted from (NH₄)₆Mo₇O₂₄ · 4H₂O plus a potassium salt and is calculated as MoO₃ + K₂O, while the transitional metal oxide and cerium oxide promoter is calculated by mass as MO_x; the proportions by weight of the various components in the catalyst are K₂MoO₄ / MO_x / carrier = (0.05-0.80) / (0.01-0.10) / 1 or MoO₃ / K₂O / MO_x / carrier = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1; before use, the catalyst is first reduced using H₂ or H₂ + CO gas at 300-350°C for 8 h, and the usage conditions for the catalyst are: volumetric proportions of the components in the feed gas CO : H₂S = 1 / (3-0.1), reaction temperature 220-350°C, pressure 0.1-2.0 MPa, reaction gas volumetric spatial velocity (2-5) × 10³h⁻¹.

2. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the said potassium salt is selected from KOH, K₂CO₃, KAc, K₂C₂O₄ or KNO₃.

3. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the said transitional metal oxide is the oxide of Fe, Co, Ni or Mn.

4. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claims 1 and 3, characterized in that the precursor of the said transitional metal oxide or cerium oxide is the respective nitrate or acetate.

5. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the proportions by mass of the components of the catalyst are $K_2MoO_4 / MO_x / \text{carrier} = (0.1-0.5) / (0.01-0.06) / 1$ or $MoO_3 / K_2O / MO_x / \text{carrier} = (0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$.

6. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the proportions by volume of the components in the feed gas are $CO : H_2S = 1 / (3-1)$.

7. Method of preparing the catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide, characterized in that the preparation of the said catalyst is by a step-by-step soaking method:

(1) A measured amount of carrier is soaked in a measured amount of an aqueous solution of a soluble salt of the selected transitional metal and/or Ce for a soaking time of 4-6 h, followed by heat drying at 100-135°C for 2-4 h and finally calcination at 500-600°C for 4-6 h, to form an intermediate modified by the transitional metal oxide and/or cerium oxide;

(2) When the active ingredient precursor is K_2MoO_4 , the intermediate prepared by modification with the transitional metal oxide and/or cerium oxide from step (1) is soaked in a measured amount of K_2MoO_4 aqueous solution according to the formulation proportions of

the catalyst for a soaking time of 4-6 h, followed by heat drying at 110-130°C for 2-4 h and finally calcination at 400-550°C for 3-5 h; when the active ingredient precursor is $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ plus a potassium salt, the intermediate prepared by the modification by the transitional metal oxide and/or cerium oxide from step (1) is soaked in a measured amount of a potassium salt solution according to the formulation proportions of the catalyst for a soaking time of 4-6 h, followed by heat drying at 100-130°C for 2-4 h, after which the carrier modified by the transitional metal oxide and/or cerium oxide and potassium salt is soaked in a measured amount of an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ according to the formulation proportions of the catalyst for a soaking time of 5-8 h, followed by heat drying at 110-130°C for 2-4 h and finally calcination at 400-550°C for 3-5 h.

Description

A Catalyst for the Synthesis of Methyl Mercaptan
through the Reaction of Carbon Monoxide with Hydrogen
Sulphide

Technical Field

This invention relates to a catalyst for the synthesis
of methyl mercaptan by a reaction of carbon monoxide
(CO) with hydrogen sulphide (H_2S). The said catalyst is
a supported Mo-O-K based complex system with at least
one transitional metal oxide and/or cerium oxide as
promoter.

Prior Art

Methyl mercaptan is a major chemical engineering
intermediate used for the synthesis of protein amino
acids, medical drugs and agrochemicals. Existing
technical routes for the synthesis of methyl mercaptan
include: a route for the synthesis of methyl mercaptan
from the reaction of methanol with hydrogen sulphide
disclosed in American patents US 5977011 and
US 6198003, European patents EP 0564706A and EP
1005906, Japanese laid-Open patent JP 219673 (2000),
the main catalyst system being $WO_3-K_2O / \gamma-Al_2O_3$ and MgO
+ $ZrO / \gamma-Al_2O_3$; a route for the direct synthesis of
methyl mercaptan from H_2S and synthesis gas ($CO + H_2$) as
starting materials as disclosed in Chinese patents ZL
98118186.4 and ZL 98118187.2, the catalyst for which
was a supported Mo-S-K based complex catalyst,
characterized by a relatively high methyl mercaptan
selectivity and space time yield; and a scheme for the
direct synthesis of methyl mercaptan from carbon
monoxide and hydrogen sulphide as disclosed in American
patents US 4668825 and US 4570020, the catalyst system
used being a catalyst of V, Nb and Ta oxides supported

on a TiO_2 carrier, this catalyst system giving a maximum CO conversion rate of 36% at 300°C .

Scope of Invention

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The objective of this invention is to provide a new catalyst system for the direct synthesis of methyl mercaptan from carbon monoxide and hydrogen sulphide. This catalyst system is a supported Mo-O-K based complex system with at least one oxide of a transitional metal and/or cerium oxide as promoter.

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The said catalyst of this invention is a catalyst system for the direct synthesis of methyl mercaptan from carbon monoxide and hydrogen sulphide, comprising an active ingredient, promoter and carrier, the said active ingredient being an Mo-O-K based complex, the promoter being at least one oxide of a transitional metal and/or cerium oxide (CeO_2), and the carrier being SiO_2 . The said active ingredient Mo-O-K based complex can be obtained by the conversion of the precursor K_2MoO_4 and is calculated as K_2MoO_4 , or is converted from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ plus a potassium salt and is calculated as $\text{MoO}_3 + \text{K}_2\text{O}$, the said potassium salt being selected from KOH , K_2CO_3 , KAc , $\text{K}_2\text{C}_2\text{O}_4$ or KNO_3 ; the said transitional metal oxide is the oxide of Fe, Co, Ni or Mn, and the precursor of the transitional metal oxide or cerium oxide is the respective nitrate or acetate; the oxide promoter is calculated as MO_x (weight), and if there is more than one oxide, MO_x represents the total of the various oxides. The proportions by weight of the various components in the catalyst are $\text{K}_2\text{MoO}_4 / \text{MO}_x / \text{carrier} = (0.05-0.80) / (0.01-0.10) / 1$ and preferably $(0.1-0.5) / (0.01-0.06) / 1$ or $\text{MoO}_3 / \text{K}_2\text{O} / \text{MO}_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$ and preferably $(0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$.

Preparation of the catalyst is by a step-by-step soaking method as follows:

(1) A measured amount of the selected transitional metal and/or Ce soluble salt is dissolved in a fixed volume of distilled water to form an aqueous solution of a certain concentration, but it is also possible to measure out a certain volume of a solution of a transitional metal and/or Ce soluble salt of known concentration, and this solution is then used to soak a measured amount of carrier; if the promoter is not limited to one kind, the separate aqueous solutions should first be made up and then combined to form a mixed aqueous solution, which is then used for soaking a measured amount of the carrier for a soaking time of 4-6 h, followed by heat drying at 100-135°C for 2-4 h and finally calcination at 500-600°C for 4-6 h, to form an intermediate modified by the transitional metal oxide and/or cerium oxide.

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(2) When the active ingredient precursor is K_2MoO_4 , a measured amount of K_2MoO_4 is dissolved in a measured volume of distilled water to form an aqueous solution of K_2MoO_4 of a certain concentration, and this solution is then used to soak the carrier prepared in step (1) and modified by the transitional metal oxide and/or cerium oxide for a soaking time of 5-8 h, followed by heat drying at 110-130°C for 2-4 h and finally calcination at 400-550°C for 3-5 h;

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When the active ingredient precursor is $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ plus a potassium salt, a measured amount of the selected potassium salt is first dissolved in a certain volume of distilled water to form a potassium salt solution of a certain concentration, and this solution is then used to soak the carrier prepared in step (1) and modified by the transitional metal oxide and/or cerium oxide for a soaking time of 4-6 h, followed by heat drying at 100-130°C for 2-4 h; the same method is

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used to dissolve a measured amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in a certain volume of distilled water to form an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ of a certain concentration, and this solution is then used to soak the carrier modified by the transitional metal oxide and/or cerium oxide and the potassium salt for a soaking time of 5-8 h, followed by heat drying at 110-130°C for 2-4 h, and finally calcination at 400-550°C for 3-5 h.

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Before use, the catalyst must first be reduced using H_2 or $\text{H}_2 + \text{CO}$ gas for 8 h at 300-350°C. The conditions for using the catalyst of this invention are: proportions by volume of the various components of the feed gas $\text{CO} : \text{H}_2\text{S} = 1 / (3-0.1)$ and preferably $1 / (3-1)$, reaction temperature 220-350°C, pressure 0.1-2.0 MPa, and volumetric spatial velocity of reaction gas (GHSV) $(2-5) \times 10^3 \text{h}^{-1}$.

20 This invention was assessed in a fixed bed tubular fluid reaction system. The feed gas and reaction products were analysed by gas chromatography, and samples were analysed 2 h after the reaction had reached a stable state. This invention has a very high activity and selectivity in the formation of methyl mercaptan, and under the assessment conditions for this invention, the CO conversion rate was 45% - 90%, the methyl mercaptan space time yield was $0.8 \text{ g.h}^{-1} \cdot \text{ml}^{-1}_{\text{cat}}$, and the selectivity reached 99%.

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Embodiments

This invention is further described below through practical examples.

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Practical Example 1

10.0 g of SiO_2 (grade 80-100) were soaked in 20 ml of an aqueous solution of $\text{Fe}(\text{NO}_3)_3$ with a concentration of

0.25 M for 4 h and this was then heat dried at 110°C for 3 h and calcined at 550°C for 4 h, to form an Fe_2O_3 / SiO_2 intermediate; 5.025 g of K_2MoO_4 were dissolved in 20 ml of distilled water to form an aqueous solution which was then used to soak the prepared Fe_2O_3 / SiO_2 intermediate for 8 h, followed by heat drying at 110°C for 3 h and calcination at 500°C for 4 h; the proportions by weight of the various components of the catalyst were K_2MoO_4 / Fe_2O_3 / SiO_2 = 0.5 / 0.04 / 1.

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Practical Example 2

0.5 g of the catalyst prepared in Practical Example 1 was placed in a stainless steel tubular reactor and was reduced with H_2 at 350°C for 8 h, after which the feed gas was introduced to conduct the reaction, the proportions by volume of the various components of the feed gas being $\text{CO} : \text{H}_2\text{S} = 1 / 1$; reaction temperature: 295°C; pressure: 0.2 MPa; spatial velocity: $3 \times 10^3 \text{h}^{-1}$. A sample was taken 2 h after the reaction had reached a stable state and was analysed by chromatography. See Table 1 (column A) for the analytical results.

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Practical Example 3

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0.5 g of the catalyst prepared in Practical Example 1 was placed in a stainless steel tubular reactor and was reduced with H_2 at 330°C for 8 h, after which the feed gas was introduced to conduct the reaction, the proportions by volume of the various components of the feed gas being $\text{CO} : \text{H}_2\text{S} = 1 / 3$; reaction temperature: 300°C; pressure: 0.6 MPa; spatial velocity: $3 \times 10^3 \text{h}^{-1}$. A sample was taken 2 h after the reaction had reached a stable state and was analysed by chromatography. See Table 1 (column B) for the analytical results.

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Practical Example 4

"18 ml of 0.20M $\text{Mn}(\text{NO}_3)_2$ solution" replaced the "20 ml of an aqueous solution of $\text{Fe}(\text{NO}_3)_3$ with a concentration of 0.25M" in Practical Example 1, while the remainder of the method was as in Practical Example 1. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

Practical Examples 5-7

The "20 ml of an aqueous solution of $\text{Fe}(\text{NO}_3)_3$ with a concentration of 0.25M" in Practical Example 1 was changed to taking 1.20 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.20 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.65 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ respectively and dissolving each in 20 ml of distilled water. These were combined to form mixed solutions, while the remainder of the preparation method was the same as the steps in Practical Example 1. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

Practical Example 8

0.500 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 15 ml of distilled water to form an aqueous solution of $\text{Ce}(\text{NO}_3)_3$, and this was combined with 10 ml of a 0.5M $\text{Fe}(\text{NO}_3)_3$ aqueous solution to form a mixed solution, while the remainder of the method was the same as the steps in Practical Example 1. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

Practical Example 9

A solution made up by dissolving 1.250 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 10 ml of distilled water was combined
5 with a solution made up by dissolving 0.500 g of $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ in 15 ml of distilled water, and this solution was used to soak 10.0 g of SiO_2 for 5 h, followed by heat drying at 110°C for 4 h and calcination at 550°C for 4 h to form an Fe_2O_3 / NiO /
10 SiO_2 intermediate, which was in turn soaked in a solution of 2.505 g of K_2MoO_4 dissolved in 20 ml of distilled water for 6 h, followed by heat drying at 120°C for 3 h and calcination at 500°C for 4 h. 0.5 g of the catalyst thus prepared was assessed by the
15 method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

Practical Example 10

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The $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ in Practical Example 9 was changed to $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, while the remainder was the same as in Practical Example 9. 0.5 g of the catalyst thus prepared was assessed by the method in Practical
25 Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

Practical Example 11

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10 ml of a solution of $\text{Fe}(\text{NO}_3)_3$ with a concentration of 0.25M were diluted with 10 ml of distilled water to form an aqueous solution of ferric nitrate with a different concentration, and this solution was then
35 used to soak 10.0 g of SiO_2 (grade 80 to 100) for 4 h, and this was heat dried at 110°C for 3 h and then calcined at 550°C in a muffle furnace for 4 h to form an Fe_2O_3 / SiO_2 intermediate; the Fe_2O_3 / SiO_2 intermediate prepared in the previous step was soaked

in an aqueous solution of 3.50 g of K_2CO_3 dissolved in 20 ml of distilled water for 4 h, followed by heat drying at $120^\circ C$ for 4 h until ready for use; the next step involved soaking the Fe_2O_3 / K_2CO_3 / SiO_2 intermediate modified in the previous two steps by Fe_2O_3 and K_2CO_3 in an aqueous solution prepared by dissolving 3.71 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 25 ml of distilled water for 7 h, followed by heat drying at $110^\circ C$ for 4 h and calcination at $500^\circ C$ for 3 h. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

15 Practical Examples 12-14

The K_2CO_3 in Practical Example 11 was changed to 2.52 g of KOH, 3.08 g of KAc and 3.64 g of $K_2C_2O_4$ respectively. The remaining steps and method were the same as in Practical Example 11. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

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Practical Example 15

0.500 g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 15 ml of distilled water to form an aqueous solution of $Ce(NO_3)_3$, which was then combined with 5 ml of a 0.5M aqueous solution of $Fe(NO_3)_3$ to form a mixed solution, and 10.0 g of SiO_2 (grade 80-100) were soaked in the solution for 4 h, heat dried at $110^\circ C$ for 3 h and then calcined in a muffle furnace at $550^\circ C$ for 4 h to form an Fe_2O_3 / CeO_2 / SiO_2 intermediate; this intermediate was then soaked for 4 h in an aqueous solution of 2.50 g of K_2CO_3 dissolved in 20 ml of distilled water, followed by heat drying at $120^\circ C$ until ready for use; the next step involved soaking the Fe_2O_3 / CeO_2 / K_2CO_3 /

SiO₂ carrier modified by Fe₂O₃, CeO₂ and K₂CO₃ in the previous two steps for 8 h in an aqueous solution made by dissolving 2.28 g of (NH₄)₆Mo₇O₂₄ · 4H₂O in 25 ml of distilled water, followed by heat drying at 130°C for 2 h and calcination at 500°C for 3 h. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

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Practical Examples 16 and 17

The 0.500 g of Ce(NO₃)₃·6H₂O in Practical Example 15 was changed to 0.500 g of Ni(Ac)₂·4H₂O and 0.500 g of Co(Ac)₂·4H₂O respectively, while the remaining steps and method were the same as in Practical Example 15. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

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Table 1. Compositions and Activity Assessment Results of the Catalysts in Practical Examples 1-10

Practical Example	Catalyst composition (active ingredient calculated as K ₂ MoO ₄)	CO conversion rate %		CH ₃ SH selectivity %***		CH ₃ SH space-time yield (g h ⁻¹ ml ⁻¹ cat)	
		A *	B **	A *	B **	A *	B **
1	K ₂ MoO ₄ /Fe ₂ O ₃ /SiO ₂ = 0.5/0.04/1	59.0	71.5	99.0	99.3	0.52	0.68
4	K ₂ MoO ₄ /MnO ₂ /SiO ₂ = 0.5/0.03/1	45.8	48.6	97.3	98.5	0.42	0.45
5	K ₂ MoO ₄ /NiO/SiO ₂ = 0.5/0.031/1	72	86.5	99.1	99.6	0.71	0.80
6	K ₂ MoO ₄ /CoO/SiO ₂ = 0.5/0.031/1	67	87	99.4	99.7	0.63	0.80
7	K ₂ MoO ₄ /CeO ₂ /SiO ₂ = 0.5/0.025/1	50	68	99.0	99.3	0.47	0.51
8	K ₂ MoO ₄ /CeO ₂ /Fe ₂ O ₃ /SiO ₂ = 0.5/0.02/0.02/1	59.2	72	99.1	99.4	0.53	0.69
9	K ₂ MoO ₄ /NiO /Fe ₂ O ₃ /SiO ₂ = 0.25/0.03/0.015/1	68	90	99.2	99.5	0.65	0.84
10	K ₂ MoO ₄ /CoO /Fe ₂ O ₃ /SiO ₂ = 0.25/0.03/0.015/1	67	88	99.0	99.3	0.64	0.81

25

Table 2. Compositions and Activity Assessment Results
of the Catalysts in Practical Examples 11-17

Practical Example	Catalyst composition (active ingredient calculated as MoO ₃ and K ₂ O)	CO conversion rate %		CH ₃ SH selectivity %***		CH ₃ SH space- time yield (g h ⁻¹ ml ⁻¹ cat)	
		A *	B **	A *	B **	A *	B **
11	MoO ₃ /K ₂ O/Fe ₂ O ₃ /SiO ₂ = 0.3/0.21/0.02/1	55.0	65.2	98.0	98.4	0.45	0.55
12	MoO ₃ /K ₂ O/Fe ₂ O ₃ /SiO ₂ = 0.3/0.21/0.02/1	56.3	66.0	99.0	99.2	0.46	0.57
13	MoO ₃ /K ₂ O/Fe ₂ O ₃ /SiO ₂ = 0.3/0.21/0.02/1	45.6	50.7	90.0	92.1	0.38	0.41
14	MoO ₃ /K ₂ O/Fe ₂ O ₃ /SiO ₂ = 0.3/0.21/0.02/1	49.0	50.2	93.3	94.2	0.45	0.50
15	MoO ₃ /K ₂ O/Fe ₂ O ₃ /CeO ₂ /SiO ₂ = 0.18/0.17/0.02/0.02/1	50.0	65.0	98.1	98.6	0.46	0.57
16	MoO ₃ /K ₂ O/Fe ₂ O ₃ /NiO/SiO ₂ = 0.18/0.17/0.02/0.015/1	58.5	68.2	98.3	98.9	0.51	0.59
17	MoO ₃ /K ₂ O/Fe ₂ O ₃ /CoO/SiO ₂ = 0.18/0.17/0.02/0.015/1	57.3	65.5	98.1	98.7	0.50	0.57

5 * Assessment results under the assessment conditions of
Practical Example 2

** Assessment results under the assessment conditions
of Practical Example 3

*** CO₂ not counted in selectivity

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the Chinese and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in China on October 10, 2003 under the number 2003101004957 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group Ltd

The 7th day of July 2008

11 November 2004

CERTIFICATE

The appendix to this certificate is a copy of the following
patent application submitted to this office

Received 06 December 2004

WIPO PCT

Date of filing: 10.10.2003

Application No.: 2003101004957

Type of application: invention

Title of invention/creation: a catalyst for the single-step
preparation of methyl mercaptan from synthesis gas containing
a high concentration of hydrogen sulphide

Applicant: Xiamen University

Inventors or designers: Yang Yiquan, Wang Qi, Lin Rencun,
Zhang Hongbin, Yuan Youzhu, Fang Weiping, Zheng Quanxing, Dai
Shenjun, Yan Xingguo

Priority

Document

Submitted or transmitted in compliance
with Rule 17.1 (a) or (b)

Commissioner of the State Intellectual Property Office of the
People's Republic of China: Wang Jingchuan

11 October 2004

Claims

1. A catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, the catalyst being composed of an active component, active promoter and carrier, characterized in that the said active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated on the basis of K_2MoO_4) or ammonium molybdate plus potassium salt or molybdenum oxide with the addition of a potassium salt (active component calculated on the basis of MoO_3 and K_2O); the active promoter is an oxide selected from that of a transitional metal or lanthanum series rare earth element with measurement expressed as MO_x , and the carrier is selected from silica or titanium oxide; the proportions by weight of the components making up the catalyst calculated on the basis of K_2MoO_4 as the active component are $K_2MoO_4 / MO_x / \text{carrier} = (0.01-0.80) / (0.001-0.01) / 1$, and the proportions by weight of the components making up the catalyst calculated on the basis of MoO_3 and K_2O as the active component are $MoO_3 / K_2O / MO_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$.

25

2. Catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that the said transitional metal or lanthanum series rare earth element oxide is the oxide of iron, manganese, cobalt, nickel, lanthanum or cerium.

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3. Catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that the proportions by weight of the components making up the catalyst calculated on

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the basis of K_2MoO_4 as the active component are $K_2MoO_4 / MO_x / \text{carrier} = (0.10-0.60) / (0.01-0.06) / 1$.

4. Catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that the proportions by weight of the components making up the catalyst calculated on the basis of MoO_3 and K_2O as the active component are $MoO_3 / K_2O / MO_x / \text{carrier} = (0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$.

5. Preparation method for a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, characterized in that the steps are as follows:

1) A nitrate of the selected transitional metal or lanthanum series rare earth element is weighed out and dissolved in distilled water to form a solution, which is then used for soaking a measured amount of the selected carrier for 3-5 h, and this is then heat-dried at $100-130^\circ\text{C}$ for 1-3 h ready for use;

2) The selected active component precursor K_2MoO_4 or $(NH_4)_6Mo_7O_{24}$ plus a potassium salt or MoO_3 plus a potassium salt are weighed out, and after dissolving in distilled water are used to soak the carrier modified as in step (1) for 7-9 h, which is heat-dried at $100-130^\circ\text{C}$ and calcined at $400-500^\circ\text{C}$ for 2-4 h.

6. Preparation method for a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 5, characterized in that the catalyst preparation method used when the precursor of the active component is $(NH_4)_6Mo_7O_{24}$ and a potassium salt is a multi-step soaking process for step 2, namely first dissolving the measured potassium salt in

distilled water and using it to soak the carrier modified by a metallic oxide for 1-3 h and heat-drying at 100-130°C, followed by dissolving a measured amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in distilled water and then using this to

5 soak the carrier modified by the potassium salt for 7-9 h, heat-drying at 100-130°C and calcining at 400-500°C for 2-4 h.

Description

Catalyst for the Single-Step Preparation of Methyl Mercaptan from Synthesis Gas Containing a High Concentration of Hydrogen Sulphide

(1) Technical Field

This invention relates to a supported catalyst used for the single-step synthesis of methyl mercaptan (CH_3SH) from synthesis gas ($\text{CO} + \text{H}_2$) with a high concentration of H_2S as the starting material, and a method for its preparation.

(2) Prior Art

Methyl mercaptan is an important chemical engineering starting material for synthesizing protein amino acids, medical drugs and agrochemicals, and the traditional method for its manufacture is through the action of potassium hydrosulphide on a halogenated methane. Other synthesis routes have subsequently been developed, such as American patent US appl. 856,232, which disclosed a reaction of hydrogen sulphide with methanol or ethyl ether to form methyl mercaptan; French patent FR appl. 93,112,491, which disclosed a method involving the hydrogenation of methylthioether for the preparation of methyl mercaptan using a transitional metal as catalyst; European patent EP 167,354, which disclosed a method for the preparation of methyl mercaptan using hydrogen sulphide and carbon monoxide as the starting material and with titanium oxide as the carrier and nickel oxide or molybdenum oxide as the active component. Chinese patents ZL 98118186.4 and ZL 98118187.2 disclosed a catalyst for the manufacture of methyl mercaptan from a synthesis gas containing a high concentration of H_2S , the active component being an Mo-S-K group produced by the conversion of a precursor K_2MoS_4 or $(\text{NH}_4)_2\text{MoS}_4$ plus a potassium salt. The space-

time yield of methyl mercaptan with this catalyst was relatively low ($0.08-0.19 \text{ g} \cdot \text{h}^{-1} \cdot \text{ml}^{-1}_{\text{cat}}$), the preparation of the precursor was also very difficult, and water could not be used as the carrier solvent, requiring the use of DMF, so that the manufacturing cost of the catalyst was high.

(3) Scope of Invention

- 10 The objective of this invention is to provide a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide as starting material and which features cheap starting materials, simple preparation, a high methyl mercaptan space-time yield and relatively high activity and selectivity.

The catalyst of this invention comprises an active component, active promoter and carrier. The active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated as K_2MoO_4) or ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$ plus a potassium salt or molybdenum oxide (MoO_3) plus a potassium salt (active component calculated as MoO_3 and K_2O); the active promoter is an oxide selected from that of a transitional metal or lanthanum series rare earth element and in particular iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), lanthanum (La) or cerium (Ce) oxide with the amount expressed as MO_x ; the carrier is selected from silica (SiO_2) or titanium oxide (TiO_2); the proportions by weight of the components making up the catalyst calculated on the basis of K_2MoO_4 as the active component are $\text{K}_2\text{MoO}_4 / \text{MO}_x / \text{carrier} = (0.01-0.80) / (0.001-0.01) / 1$, and preferably $(0.10-0.60) / (0.01-0.06) / 1$; and if calculated with MoO_3 and K_2O as the active component, the proportions by weight in the catalyst are $\text{MoO}_3 / \text{K}_2\text{O} / \text{MO}_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$, and preferably $(0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$.

The preparation method for the catalyst is as follows:

1) A nitrate of the selected transitional metal or
5 lanthanum series rare earth element is weighed out and
dissolved in distilled water to form a solution, which
is then used for soaking a measured amount of the
selected carrier for 3-5 h, and this is then heat-dried
at 100-130°C for 1-3 h ready for use;

10

2) The selected active component precursor (K_2MoO_4
or $(NH_4)_6Mo_7O_{24}$ plus a potassium salt or MoO_3 plus a
potassium salt) is weighed out, and after dissolving in
distilled water is used to soak the carrier modified as
15 in step (1) for 7-9 h, which is heat-dried at 100-130°C
and calcined at 400-500°C for 2-4 h.

A multi-step soaking method can also be used when the
active component precursor is $(NH_4)_6Mo_7O_{24}$ and a
20 potassium salt, namely by first dissolving the measured
potassium salt in distilled water and using it to soak
the carrier modified by a metallic oxide for 1-3 h and
heat-drying at 100-130°C, followed by dissolving a
measured amount of $(NH_4)_6Mo_7O_{24}$ in distilled water and
25 then using this to soak the carrier modified by the
potassium salt for 7-9 h, heat-drying at 100-130°C and
calcining at 400-500°C for 2-4 h.

Assessment of catalyst activity is carried out in a
30 fluid reaction system on a fixed bed, with the
composition of the starting material gas being
(proportions by volume) $CO/H_2/H_2S = 1/2/(0.1-1)$, the
reaction temperature 220-350°C, the pressure 0.1-2.0
MPa, spatial velocity $(2-5) \times 10^3 h^{-1}$. The compositions
35 of the starting material gas and product are determined
by gas chromatography. The catalyst is first reduced
for 8 h by H_2 at 300-350°C, after which starting
material gas is passed in for 8 h followed by
measurement of product composition.

As is generally known, the properties and performance of a catalyst are determined by the starting materials for its manufacture and the manufacturing method (including process conditions). When the catalyst contains a certain element, for example Mo, it is in principle possible to select all simple substances or compounds containing the element Mo as one of the starting materials for manufacture of this catalyst. However, different starting materials inevitably introduce other different groups or atoms, so that when selecting MoO_3 , O atoms are introduced, while when selecting ammonium molybdate, O atoms and NH_4^+ groups are introduced. These other introduced groups will affect the physical changes and chemical changes which occur during the catalyst manufacturing process, and thus finally result in differences in the properties and performance of the catalyst. This invention prepares a catalyst with high activity and selectivity through the selection of appropriate starting materials containing Mo and K, and under the assessment conditions of this invention, the space-time yield of methyl mercaptan was $0.27\text{--}0.33 \text{ g}\cdot\text{h}^{-1}\cdot\text{ml}^{-1}_{\text{cat}}$, and selectivity reached 92.7% - 98.6%. Furthermore, the selected starting materials are cheap and readily obtainable, and the manufacturing process is simple and convenient.

(4) Embodiments

This invention is further described below by means of practical examples.

Practical Example 1. 0.725 g of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was weighed out and dissolved in 20 ml of distilled water to make up a ferric nitrate solution, which was used to soak 10.0 g of SiO_2 (grade 80-100) for 4 h, and this was heat-dried at 110°C for 2 h. It was then calcined in a muffle furnace at 500°C for 4 h and cooled ready for

use. 5.0 g of K_2MoO_4 was weighed out and dissolved in 20 ml of distilled water to form an aqueous solution of K_2MoO_4 , which was used to soak 10 g of SiO_2 modified with Fe as described above for 8 h. It was heat-dried at 110°C for 2 h and calcined at 500°C for 4 h. The catalyst thus prepared had a composition by weight of K_2MoO_4 / Fe_2O_3 / SiO_2 = 0.5 / 0.03 / 1. See Table 1 for the activity assessment results.

10 Practical Example 2. The carrier used in Practical Example 1 was changed to TiO_2 , while the remainder of the preparation method was the same as in Practical Example 1, and the composition and assessment results for the catalyst obtained are shown in Table 1.

15

Practical Example 3. 20 ml of distilled water was added to 0.58 ml of a 50% solution by weight of $Mn(NO_3)_2$ to form a manganese nitrate solution, while the remainder of the method was as in Practical Example 1. The catalyst thus prepared had proportions by weight of K_2MoO_4 / MnO_2 / SiO_2 = 0.5 / 0.025 / 1, and the activity assessment results are shown in Table 1.

25 Practical Examples 4-7. The "0.725 g of $Fe(NO_3)_3 \cdot 9H_2O$ " in Practical Example 1 was changed to 1.16 g of $Ni(NO_3)_2 \cdot 6H_2O$, 1.16 g of $Co(NO_3)_2 \cdot 6H_2O$, 0.67 g of $La(NO_3)_3$ and 0.66 g of $Ce(NO_3)_3 \cdot 6H_2O$ respectively, while the remainder of the preparation was as in Practical Example 1. See Table 1 for the composition and activity assessment results of the catalysts obtained.

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Table 1. Composition and Activity Assessment Results
for the Catalysts in Practical Examples 1-7 *

Practical Example	Catalyst composition (W) (active component Mo-O-K calculated as K_2MoO_4)	CH_3SH selectivity (%)	CH_3SH space-time yield ($g h^{-1} ml^{-1}_{cat}$)
1	$K_2MoO_4/Fe_2O_3/SiO_2 = 0.5/0.03/1$	98.6	0.33
2	$K_2MoO_4/MnO_2/SiO_2 = 0.5/0.03/1$	98.5	0.32
3	$K_2MoO_4/MnO_2/TiO_2 = 0.5/0.05/1$	92.7	0.29
4	$K_2MoO_4/NiO/SiO_2 = 0.5/0.03/1$	94.8	0.31
5	$K_2MoO_4/CoO/SiO_2 = 0.5/0.03/1$	98.6	0.32
6	$K_2MoO_4/La_2O_3/SiO_2 = 0.5/0.03/1$	98.6	0.32
7	$K_2MoO_4/CeO_2/SiO_2 = 0.5/0.03/1$	97.6	0.31

* assessment conditions: high sulphur synthesis gas composition in proportions by volume of $CO/H_2/H_2S = 1/2/1$, reaction temperature $295^\circ C$, pressure 0.2 MPa, spatial velocity $3 \times 10^3 h^{-1}$.

Practical Example 8. 0.725 g of $Fe(NO_3)_3 \cdot 9H_2O$ was weighed out and dissolved in 20 ml of distilled water to make up a ferric nitrate solution, which was used to soak 10.0 g of SiO_2 (grade 40-60) for 4 h, and this was heat-dried at $110^\circ C$ for 2 h. It was then calcined in a muffle furnace at $550^\circ C$ for 4 h ready for use. 2.67 g of K_2CO_3 was weighed out and dissolved in 20 ml of distilled water. This was then used to soak the SiO_2 carrier modified with iron as described above for 4 h, which was heat-dried at $110^\circ C$ ready for use. 3.60 g of $(NH_4)_6Mo_7O_{24}$ was weighed out and dissolved in 25 ml distilled water, which was used to soak the Fe_2O_3/SiO_2 carrier modified with K_2CO_3 for 8 h. It was heat-dried at $110^\circ C$ and calcined at $550^\circ C$ for 2 h. See Table 2 for the composition and activity assessment results of the catalyst obtained.

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Practical Example 9. The 2.67 g of K_2CO_3 from Practical Example 8 was changed to 1.8 g of KOH, while the remainder of the preparation method was as in Practical

Example 8. See Table 2 for the composition and activity assessment results of the catalyst obtained.

5 Practical Example 10. The $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in Practical Example 9 was changed to 3.0 g of MoO_3 , while the remainder of the preparation method was as in Practical Example 8. See Table 2 for the composition and activity assessment results of the catalyst obtained.

10 Table 2. Composition and Activity Assessment Results for the Catalysts in Practical Examples 8-10 *

Practical Example	Catalyst composition (W) (active component Mo-O-K calculated as $\text{MoO}_3/\text{K}_2\text{O}$)	CH_3SH selectivity (%)	CH_3SH space-time yield ($\text{g h}^{-1} \text{ml}^{-1}_{\text{cat}}$)
8	$\text{MoO}_3/\text{K}_2\text{O}/\text{Fe}_2\text{O}_3/\text{SiO}_2 = 0.3/0.15/0.03/1$	98.5	0.31
9	$\text{MoO}_3/\text{K}_2\text{O}/\text{Fe}_2\text{O}_3/\text{SiO}_2 = 0.3/0.15/0.03/1$	98.6	0.30
10	$\text{MoO}_3/\text{K}_2\text{O}/\text{Fe}_2\text{O}_3/\text{SiO}_2 = 0.3/0.15/0.03/1$	94.1	0.27

* assessment conditions: $\text{CO}/\text{H}_2/\text{H}_2\text{S} = 1/2/1$, (V), 0.2 MPa, $3 \times 10^3 \text{ h}^{-1}$, 295°C .

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the Chinese and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in China on October 10, 2003 under the number 2003101004961 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group Ltd

The 7th day of July 2008

Claims

1. Catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, the said catalyst including a carrier and an active component, characterized in that the carrier is selected from silica, titanium oxide or a heavy rare earth oxide; the active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated as K_2MoO_4) or ammonium molybdate plus a potassium salt or molybdenum oxide plus a potassium salt (active component calculated as MoO_3 and K_2O); when the active component is calculated as K_2MoO_4 , the proportions by weight of the components in the catalyst are K_2MoO_4 /carrier = (0.01-0.80)/1; and when the active component is calculated as MoO_3 and K_2O , the proportions by weight of the components in the catalyst are MoO_3/K_2O /carrier = (0.01-0.80)/(0.01-0.50)/1.

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2. Catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that when the active component is calculated as K_2MoO_4 , the proportions by weight of the components in the catalyst are K_2MoO_4 /carrier = (0.10-0.60)/1.

25

3. Catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that when the active component is calculated as MoO_3 and K_2O , the proportions by weight of the components in the catalyst are MoO_3/K_2O /carrier = (0.10-0.50)/(0.10-0.30)/1.

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4. A method for preparing a catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, characterized in that the steps are dissolving a measured amount of

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the precursor of the Mo-O-K based complex active component in distilled water and soaking a measured amount of the selected carrier in this for 7-9 h, heat drying at 100-130°C and calcination at 400-500°C for 2-5 4 h.

Description

A Catalyst for the Synthesis of Methyl Mercaptan from
Synthesis Gas Containing a High Concentration of
Hydrogen Sulphide

(1) Technical Field

This invention relates to a supported catalyst for
the single-step synthesis of methyl mercaptan (CH_3SH)
from synthesis gas ($\text{CO} + \text{H}_2$) containing a high
concentration of H_2S as starting material and a method
for its preparation.

(2) Prior Art

Methyl mercaptan is an important chemical engineering
starting material for synthesizing protein amino acids,
medical drugs and agrochemicals, and the traditional
method for its manufacture is through the action of
potassium hydrosulphide on a halogenated methane. Other
synthesis routes have subsequently been developed, such
as American patent US appl. 856,232, which disclosed a
reaction of hydrogen sulphide with methanol or ethyl
ether to form methyl mercaptan; French patent FR appl.
93,112,491, which disclosed a method involving the
hydrogenation of methylthioether for the preparation of
methyl mercaptan using a transitional metal as
catalyst; European patent EP 167,354, which disclosed a
method for the preparation of methyl mercaptan using
hydrogen sulphide and carbon monoxide as the starting
material and with titanium oxide as the carrier and
nickel oxide or molybdenum oxide as the active
component. Chinese patents ZL 98118186.4 and
ZL 98118187.2 disclosed a catalyst for the manufacture
of methyl mercaptan from a synthesis gas containing a
high concentration of H_2S , the active component being an
Mo-S-K group produced by the conversion of a precursor
 K_2MoS_4 or $(\text{NH}_4)_2\text{MoS}_4$ plus a potassium salt. The space-

time yield of methyl mercaptan with this catalyst was relatively low ($0.08-0.19 \text{ g}\cdot\text{h}^{-1}\cdot\text{ml}^{-1}_{\text{cat}}$), the preparation of the precursor was also very difficult, and water could not be used as the carrier solvent, requiring the use of DMF, so that the manufacturing cost of the catalyst was high.

(3) Scope of Invention

The objective of this invention is to provide a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide as starting material and which features cheap starting materials, simple preparation, a high methyl mercaptan space-time yield and relatively high activity and selectivity.

The said catalyst of this invention includes a carrier and an active component, with the carrier selected from silica (SiO_2), titanium oxide (TiO_2) or a heavy rare earth oxide; the active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated as K_2MoO_4) or ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$ plus a potassium salt or molybdenum oxide (MoO_3) plus a potassium salt (active component calculated as MoO_3 and K_2O); when the active component is calculated as K_2MoO_4 , the proportions by weight of the components in the catalyst are $\text{K}_2\text{MoO}_4/\text{carrier} = (0.01-0.80)/1$ and preferably $(0.10-0.60)/1$; and if the active component is calculated as MoO_3 and K_2O , the proportions by weight of the components in the catalyst are $\text{MoO}_3/\text{K}_2\text{O}/\text{carrier} = (0.01-0.80)/(0.01-0.50)/1$ and preferably $(0.10-0.50)/(0.10-0.30)/1$.

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The method for preparing the catalyst is: a measured amount of the precursor of the Mo-O-K based complex active component is dissolved in distilled water, and a measured amount of the selected carrier is soaked in

this for 7-9 h, heat dried at 100-130°C and calcined at 400-500°C for 2-4 h.

Assessment of catalyst activity is carried out in a fluid reaction system on a fixed bed, with the composition of the synthesis gas containing a high concentration of H₂S being (proportions by volume) CO/H₂/H₂S = 1/2/(0.1-1), reaction temperature 220-350°C, pressure 0.2-2.0 MPa, spatial velocity $(2-5) \times 10^3 \text{ h}^{-1}$. The compositions of the starting material gas and product are determined by gas chromatography. The catalyst is first reduced for 8 h by H₂ at 300-350°C, after which starting material gas is passed in for 8 h followed by measurement of product composition.

As is generally known, the properties and performance of a catalyst are determined by the starting materials for its manufacture and the manufacturing method (including process conditions). When the catalyst contains a certain element, for example Mo, it is in principle possible to select all simple substances or compounds containing the element Mo as one of the starting materials for manufacture of this catalyst. However, different starting materials inevitably introduce other different groups or atoms, so that when selecting MoO₃, O atoms are introduced, while when selecting ammonium molybdate, O atoms and NH₄⁺ groups are introduced. These other introduced groups will affect the physical changes and chemical changes which occur during the catalyst manufacturing process, and thus finally result in differences in the properties and performance of the catalyst. This invention prepares a catalyst with high activity and selectivity through the selection of appropriate starting materials containing Mo and K, and under the assessment conditions of this invention, the space-time yield of methyl mercaptan was $0.25 \text{ g} \cdot \text{h}^{-1} \cdot \text{ml}^{-1}_{\text{cat}}$, and selectivity reached 98.8%. Furthermore, the selected starting

materials are cheap and readily obtainable, and the manufacturing process is simple and convenient.

(4) Embodiments

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This invention is further described below by means of practical examples.

10 Practical Example 1. 1.0 g of K_2MoO_4 was weighed out and dissolved in 5 ml of distilled water. 2 g of SiO_2 (grade 40-60) was soaked in this for 8 h, heat dried at $110^\circ C$ for 2 h and calcined at $500^\circ C$ for 2 h. The proportions by weight of the components in the catalyst thus prepared were $K_2MoO_4/SiO_2 = 0.50/1$, and the activity
15 assessment results are shown in Table 1.

Practical Examples 2 and 3. The carrier SiO_2 in Practical Example 1 was changed to TiO_2 or a heavy rare earth oxide, with the remainder of the preparation
20 method as in Practical Example 1. The activity assessment results are shown in Table 1.

Practical Example 4. 0.72 g of $(NH_4)_6Mo_7O_{24}$ and 0.88 g of K_2CO_3 were weighed out and dissolved in 5 ml of
25 distilled water. 2 g of SiO_2 carrier was soaked in this for 8 h, heat dried at $110^\circ C$ and calcined at $450^\circ C$. The proportions by weight of the components in the catalyst prepared from this were $MoO_3/K_2O/SiO_2 = 0.30/0.30/1.0$, and its activity assessment results are shown in Table
30 1.

Practical Example 5. 0.44 g of K_2CO_3 was weighed out and dissolved in 5 ml of distilled water. 2 g of SiO_2 was soaked in this for 4 h and heat dried at $110^\circ C$. 0.72 g
35 of $(NH_4)_6Mo_7O_{24}$ was weighed out and dissolved in 5 ml of distilled water, and the SiO_2 carrier which had been modified by K_2CO_3 was soaked in this for 8 h, heat dried at $110^\circ C$ and calcined at $450^\circ C$ for 2 h. The proportions by weight of the components in the catalyst thus

prepared were $\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$, and the activity assessment results are shown in Table 1.

Practical Example 6. The 0.44 g of K_2CO_3 in Practical Example 5 was changed to 0.36 g of KOH, while the remainder of the preparation method was as in Practical Example 5. The proportions by weight of the components in the catalyst prepared were $\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$. The activity assessment results are shown in Table 1.

Practical Example 7. 0.6 g of MoO_3 and 0.36 g of KOH were weighed out and dissolved in 5 ml of distilled water. 2 g of TiO_2 (grade 40-60) carrier was soaked in this for 8 h, heat dried at 110°C and calcined at 450°C for 2 h. The proportions by weight of the components in the catalyst prepared were $\text{MoO}_3/\text{K}_2\text{O}/\text{TiO}_2 = 0.30/0.15/1$. The catalyst activity assessment results are shown in Table 1.

Table 1. Composition and Activity Assessment Results for the Catalysts in Practical Examples 1-7 *

Practical Example	Catalyst composition (proportions by weight) %	CH_3SH selectivity (%)	CH_3SH space-time yield ($\text{g h}^{-1} \text{ml}^{-1}_{\text{cat}}$)
1	$\text{K}_2\text{MoO}_4/\text{SiO}_2 = 0.5/1$	98.5	0.25
2	$\text{K}_2\text{MoO}_4/\text{TiO}_2 = 0.5/1$	98.8	0.24
3	$\text{K}_2\text{MoO}_4/\text{heavy rare earth} = 0.5/1$	98.8	0.24
4	$\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.30/1$	96.8	0.23
5	$\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$	97.2	0.24
6	$\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$	94.2	0.21
7	$\text{MoO}_3/\text{K}_2\text{O}/\text{TiO}_2 = 0.30/0.15/1$	93.5	0.18

* assessment conditions: $\text{CO}/\text{H}_2/\text{H}_2\text{S} = 1/2/1$, (V), 0.2 MPa, 295°C , $3 \times 10^3 \text{ h}^{-1}$.